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High-spin Fe(III) Schiff based complexes with photoactive ligands. Synthesis, EPR study and magnetic properties

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ABSTRACT

A series of three novel Fe(III) compounds of the formula $[FeL_2]X$ (where $X = Cl^-$ **(1)**, PF_6^- **(2)**, NO_3^- (**3**), and L is a photoactive ligand, (4)-4-(((2-(ethylamino)ethyl)imino)methyl)-3-hydroxyphenyl 4-bromobenzoate) was synthesized and studied by means of electron paramagnetic resonance (EPR) and pulsed laser irradiation. The Fe^{3+} ions in these compounds are in a high-spin state. A thorough analysis of the EPR data suggests that compounds **1** and **2** undergo an order–disorder ferroelectric phase transition, and below the phase transition temperature (T_c = 100 and 200 K for compounds **1** and **2**, respectively) a nonzero average electric dipole moment appears. To get an insight into molecular structure of Fe^{3+} ions and their supramolecular organization in low-temperature (LT) and high-temperature (HT) phases of compounds **1** and **2**, a series of density functional theory calculations was performed. On the basis of our findings, the LT- and HT-phase structures were proposed for these compounds. It was also shown that, whereas the chloride and hexafluorophosphate anions are able to form a network of hydrogen bonds between the $[FeL_2]X$ units (ionic pairs), which enable an electric dipole ordering in the sample, the nitrate anions, in contrast, tend to form hydrogen bonds inside the ionic pair. This conclusion is evidenced by the observed EPR spectra, which are different for compound **3** and are not indicative of the existence of an order–disorder ferroelectric phase transition. The EPR data obtained upon irradiation of compound **1** show that photoexcitation in the UV region at 5 K destroys hydrogen bonds and converts cationic complexes into ligand-to-metal charge transfer (LMCT) states, in which the iron is ferrous, and the unpaired electron is located on the salicylidene moieties. The LMCT states decay back to the ferric one, and ferric complexes further form the most stable (LT) phase structure.

1. Introduction

Iron(III) complexes with Schiff base ligands are widely studied due to the presence of interesting magnetic properties, in particular spin-crossover (SCO) or spin transition [1,2]. Iron(III) (d^5) centers in SCO complexes can adopt two different spin states, low-spin state (LS, $S = 1/2$) and high-spin state (HS, $S = 5/2$), and can undergo a transition from one state into another by application of the external perturbation such as temperature, pressure, light or magnetic field [3]. The vision of Kahn and co-workers on the use of SCO compounds in data processing [4] led to the appearance of impressive literature on the SCO. It includes the discovery of several new examples of SCO compounds [1,5–7], explanation of the different types of SCO profiles [8], modification of SCO compounds to increase cooperativity and to enable their application into materials science [9]. Among complexes showing SCO, $[Fe(salEen)_2]^+$ derivatives (salEen = *N*-ethyl-*N*-(2-aminoethyl)salicylaldiminate) are known to undergo a thermally induced SCO [10] and demonstrate different types of SCO profiles from gradual to abrupt, from incomplete to complete depending on the counterion. It has been found that Cl^- and NO_3^- anions tend to stabilize the LS state, while complex with BPh_4^- anion adopt preferably the HS state [10].

Interest to the study of these compounds is now increasing sharply, since Fe(III) salEen Schiff base complexes can be used as MRI contrast agents [11]. Iron is a biocompatible metal and paramagnetism is observed for both HS and LS Fe(III) species. Moreover, these complexes have protons that can easily exchange with the

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